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DEPARTMENT OF THE INTERIOR
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THE BEHAVIOR OF NITROGLYCERIN WHEN HEATED

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BY

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CONTENTS.

	Page.
Introduction	3
Previous investigations	3
Investigations by the authors	5
Apparatus used	5
The method of procedure	7
Changes observed	8
Effect of heating at constant temperature	8
Effect of heating at rising temperature	11
Summary	12
Publications on mine accidents and tests of explosives	13

ILLUSTRATIONS.

PLATE I.—Protective cabinet	6
FIGURE 1.—Apparatus for determining the explosion temperature of nitroglycerin	7
2.—Apparatus used in the distillation of nitroglycerin	9

THE BEHAVIOR OF NITROGLYCERIN WHEN HEATED.

By WALTER O. SNELLING and C. G. STORM.

INTRODUCTION.

The Bureau of Mines, under the authority of the act that established it, is conducting investigations relating to the use of explosives. These investigations include physical and chemical tests, which are carried on chiefly at the experiment station of the bureau at Pittsburgh, Pa. A study of the behavior of nitroglycerin when exposed to heat has been made in the explosives laboratory at that station and is described in this paper.

A knowledge of the action of heat upon nitroglycerin is very important, because of the information thereby gained in regard to the stability of explosives and the behavior of large masses of explosives when burning, and the relation of such facts to fires in magazines and nitroglycerin factories.

Very little information on the behavior of nitroglycerin at high temperatures is available in the literature relating to explosives. The importance of such information has been fully recognized by investigators, and a number of attempts have been made to obtain it by experimental study. Results of even approximate accuracy have been difficult to get, because of the readiness with which nitroglycerin explodes when its temperature is slightly raised and because of the destructive effects of the explosion of even very small quantities of the substance.

PREVIOUS INVESTIGATIONS.

Several investigators, notably Champion,[a] de Bruyn,[b] Hagen,[c] and Munroe,[d] have devised most ingenious methods for indirectly observing the effect of heat upon nitroglycerin, and the knowledge available at the present time in relation to this subject is derived almost entirely from the studies that have been made, at considerable personal hazard, by the investigators named.

[a] Zeitschr. für Chemie, 1871, p. 351; abstracted in Comptes Rendus, vol. 73, 1871, p. 42.
[b] Recueil des travaux chimiques des Pays-Bas, vol. 14, 1895, pp. 131–133.
[c] Referred to in Escales, Die Explosivstoffe, vol. 3, p. 160.
[d] Jour. Am. Chem. Soc., vol. 12, 1890, pp. 57–64.

The effect of temperatures below 100° C. upon nitroglycerin has been the subject of many researches, and these have given important information to manufacturers and users of explosives. The common tests (known as heat tests) for determining the stability of nitroglycerin and nitroglycerin explosives depend either upon the time required for the production from nitroglycerin (at temperatures below 100° C.) of oxides of nitrogen sufficient to color potassium-iodide-starch or other test paper, or upon the measurement in some other manner of the oxides of nitrogen evolved.

One of the early studies to determine the effect of temperatures above 100° C. upon nitroglycerin was made by Leygue and Champion [a] and by Champion.[b] The work was based upon the known distribution of temperature in a metal bar, heated at one extremity. A copper bar was used provided with cavities at equal intervals. These cavities were filled with oil or an alloy of low fusing point, and by means of thermometers placed within them the interior temperature of the bar was measured. A curve was prepared showing the temperature at all points along the bar. When equilibrium was reached, as indicated by the reading of the thermometer, small quantities of the explosive to be tested were placed at different points along the bar until the desired effects were obtained. A screen was interposed between the source of heat and the samples being tested to keep them from being affected by radiant heat. Tested in this way, nitroglycerin was found to detonate at the temperature of 256° C., and ebullition took place at the temperature of 185° C.

It is evident that the method just outlined has many serious faults, and must necessarily fail to give results that are at all accurate. Lobry de Bruyn [c] noted that it was very doubtful if the explosive could really reach the temperature of the bar, and he therefore concluded that the temperatures obtained by Leygue and Champion were really far higher than they should have been. For example, Champion had ascertained that nitrocellulose (guncotton) could be heated to 220° C. before ignition occurred, while Lobry de Bruyn failed, as most others have since done, to bring nitrocotton to a temperature higher than 190° C. without causing explosion. Lobry de Bruyn heated nitroglycerin, in quantities up to 2 cubic centimeters, in a flask immersed in a glycerin bath containing a thermometer, but in his experiments he kept the nitroglycerin under reduced pressure by means of an air pump connected to a side-necked tube of the flask, and accordingly he did not obtain results of direct value in determining the action of heat upon nitroglycerin under ordinary conditions.

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[a] Abstracted in Comptes Rendus, vol. 73, 1871, pp. 42 and 1478.

[b] Zeitschr. für Chemie, 1871, p. 351.

[c] Recueil des travaux chimiques des Pays-Bas, vol. 14, 1895, pp. 131–133; and Jahresbericht über die Fortschritt der Chemie, vol. 48, 1895, p. 1000.

Charles E. Munroe [a] found the firing temperature of nitroglycerin to be 203° to 205° C. In his experiments, the sample of explosive (one drop in the case of nitroglycerin) was placed at the bottom of a thin copper cartridge case, $\frac{5}{8}$ inch in diameter and $1\frac{5}{16}$ inches long. The copper case was then immersed in a bath of paraffin or molten tin contained in an iron vessel. The initial temperature of the bath was noted by means of a thermometer suspended at the side of the cartridge case to a depth of 1 inch (the cartridge case when put in the bath being plunged so that its lower end was also immersed to a depth of about 1 inch). The temperature of the bath was then quickly raised and the reading of the thermometer at the moment the nitroglycerin exploded was noted as the firing point. Munroe's results were as follows:

Determinations by Munroe of firing point of nitroglycerin.

Initial temperature.	Firing point.
°C.	°C.
150	204
180	203
185	204
190	205
190	205
195	205

Nobel [b] gives 180° C. as the firing point of nitroglycerin. Abel [c] states that with proper precautions nitroglycerin can be heated to 193° C. without explosion.

INVESTIGATIONS BY THE AUTHORS.

APPARATUS USED.

As a part of the equipment of the explosives laboratory of the Bureau of Mines, there has recently been constructed, from designs made by the authors, a protective cabinet (Pl. I) for the purpose of facilitating the study of explosive reactions. The cabinet, 76 centimeters (30 inches) on a side, is made of steel plates 1.9 centimeters (0.75 inch) thick. Means are provided for illuminating the interior of the cabinet, and a window of very heavy plate glass is so arranged as to permit observations being safely made of any work that is being conducted in the cabinet.

A number of experiments, intended mainly to test the resistance of the cabinet to explosive shock, showed observation to be perfectly safe through the protected window when a 2 to 3 gram quantity of nitroglycerin exploded.

The illumination of the interior of the cabinet was effected by means of a 16-c. p. incandescent electric light. When lighting from

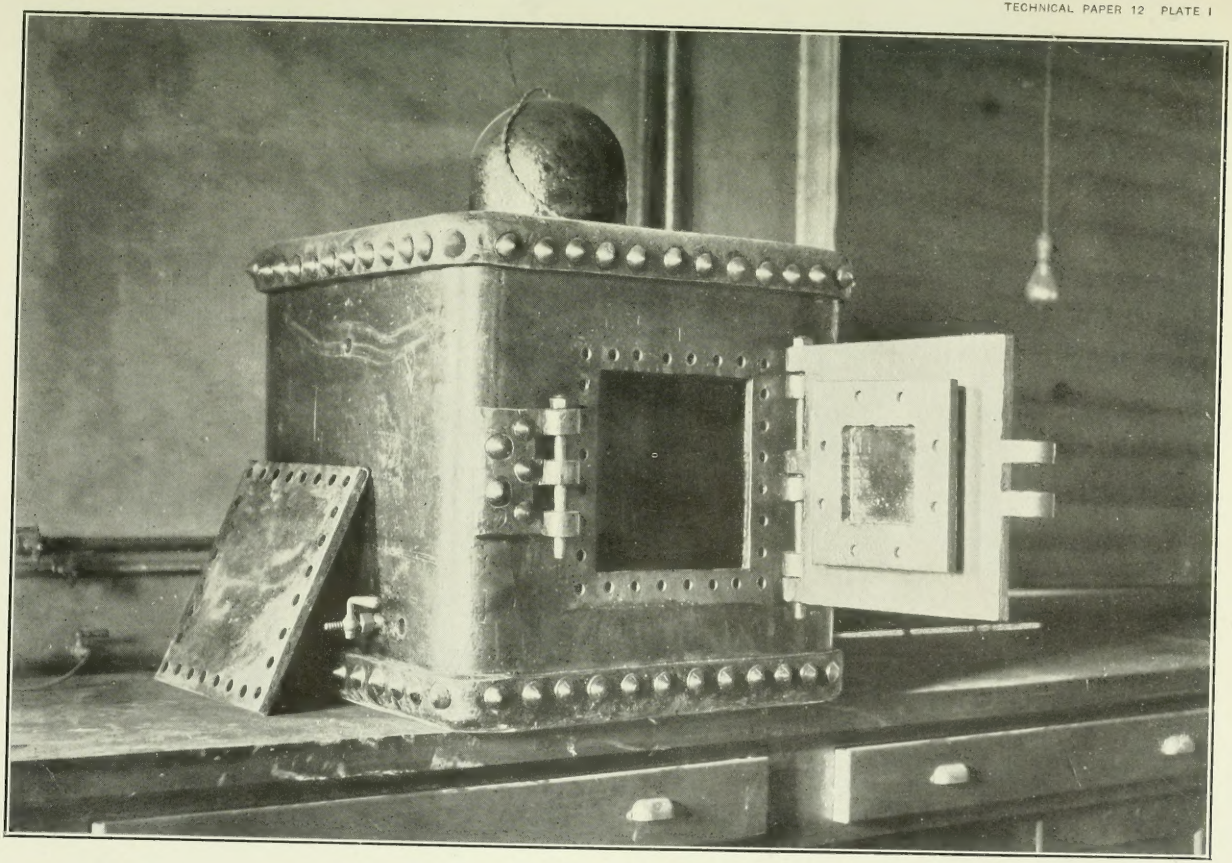
[a] Jour. Am. Chem. Soc., vol. 12, 1890, pp. 57–64.
[b] Dingler's Polyt. Jour., vol. 183, 1867, pp. 221–225.
[c] Dingler's Polyt. Jour., vol. 195, 1870, pp. 364–369.

without the chamber of the cabinet was desirable an electric light was placed in the dome of the cabinet (see Pl. I), this dome being separated from the chamber of the cabinet by a window of heavy plate glass, reinforced by a steel frame. The purpose of the dome was to prevent pieces of glass from this window from being a source of danger in the event of the window being ruptured. In many experiments a better illumination than was afforded by light admitted through the window in the top of the cabinet was desirable. Such illumination was obtained by an incandescent lamp within the chamber of the cabinet, the lamp being held in proper position by a suitable stand. With this method each explosion naturally resulted in the loss of an electric-light bulb, but the superior illumination compensated for the small cost of the broken bulbs.

The heavy plate glass of the windows was so greatly scarred after each explosion as to seriously impair its transparency. As the glass was exceptionally heavy, and therefore expensive, a means was sought by which the replacing of the heavy panes might be avoided. Complete success was obtained by placing a thin pane of ordinary glass, cut to the size of the window, on the inside of the cabinet and in contact with the plate glass. After each explosion it was only necessary to remove the pane of thin glass, which had become badly scarred, and to replace it by a new one. Thus, at a cost of 1 or 2 cents for each shot, a fully transparent window was provided.

As this cabinet seemingly offered an ideal means of conducting work that could not with any degree of safety be carried out by means heretofore at the command of experimenters, some studies were undertaken to determine the effect of temperatures between 100° and 200° C. upon pure nitroglycerin. In these experiments, to obviate the difficulties encountered by former investigators in regard to indirect measurements, such as those depending upon the distribution of heat along a metal bar, direct determinations of temperature were made, either by a thermometer that was immersed directly in the nitroglycerin under test and was observed through the plate-glass window, or by means of a thermocouple that was immersed within the nitroglycerin and was read by means of a galvanometer situated at such a distance as to be unaffected by the jar caused by the explosion.

Preliminary experiments showed that the measurement of temperature by means of the immersed thermocouple could be carried out very conveniently and with great precision. The thermocouple used was that which is commonly known as the "constantan-copper" thermocouple, one of the wires being composed of the alloy known as "constantan," and the other being of ordinary copper. Such a thermocouple is very sensitive, the wires are cheap, and after each explosion it is a very simple matter to solder together new portions of the wire to form a new junction, ready for standardization.



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In each experiment one junction of the "constantan-copper" thermocouple was immersed in the nitroglycerin under test, and the other junction of the thermocouple was wholly immersed in melting ice. The readings of the thermocouple were standardized by the use of liquids of known boiling point, liquids being selected that boil at about the same temperatures as were to be measured in the experiments.

THE METHOD OF PROCEDURE.

The method of procedure used in the study can be best explained by a general outline of some of the tests made. Usually about 2 cubic centimeters of nitroglycerin was taken, and was placed in a

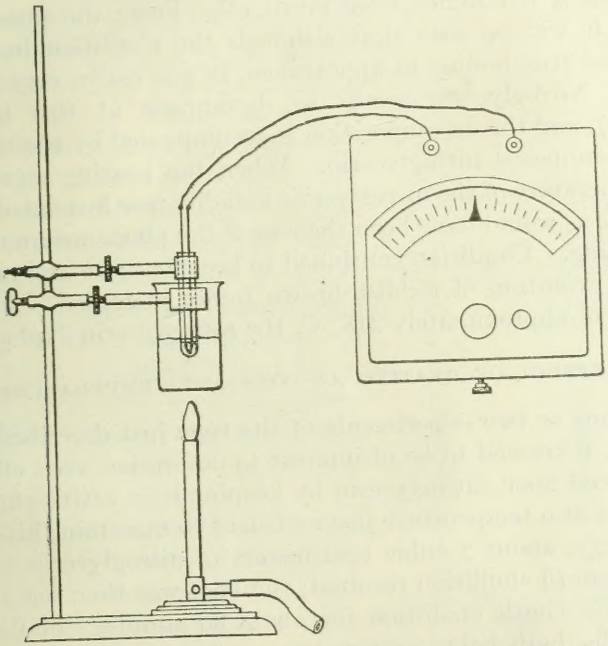

FIGURE 1.—Apparatus for determining the explosion temperature of nitroglycerin.

small test tube, held by means of a clamp in the proper position in a bath of melted paraffin. The thermocouple was placed in the nitroglycerin, and carefully adjusted in such position that the junction of the two wires was about in the center of the nitroglycerin. The arrangement of the thermocouple, test tube, and paraffin bath is shown in figure 1. The entire apparatus was then placed within the protective cabinet, and readings of the galvanometer were taken at intervals of 30 seconds.

All the changes that occurred were noted by an observer at the protected window of the cabinet, and by means of two watches carefully adjusted to run synchronously the observer at the cabinet and

the observer at the galvanometer obtained continuous records of all the successive phenomena in the course of the experiment.

CHANGES OBSERVED.

In the experiments with nitroglycerin no change was observed until the temperature of the nitroglycerin reached about 135° C. At this point the nitroglycerin became slightly more yellow in color, and as the temperature rose a rapid deepening in color was noted, until at about 140° C. the nitroglycerin was of a reddish-orange color. At about 145° C. ebullition began; small bubbles formed in all parts of the nitroglycerin and rose in a regular manner. Generally foam collected over the top of the nitroglycerin at this stage of the heating, and copious red fumes were given off. From the phenomena described it will be seen that although the ebullition in every way resembled true boiling in appearance, it was really very different in nature. Nitroglycerin seems to decompose at this temperature (145° C.), and the decomposition is accompanied by the vaporization of undecomposed nitroglycerin. When the heating was continued, the temperature of the nitroglycerin steadily rose instead of remaining constant, as would have been the case if the phenomenon represented true boiling. Ebullition continued to become more and more active, and the evolution of reddish-brown fumes increased. At the temperature of approximately 218° C. the nitroglycerin exploded.

EFFECT OF HEATING AT CONSTANT TEMPERATURE.

After one or two experiments of the type just described had been reviewed, it seemed to be of interest to determine what effect would be produced upon nitroglycerin by keeping it in active ebullition for some time at a temperature just sufficient to maintain this condition. Accordingly, about 2 cubic centimeters of nitroglycerin was heated gradually until ebullition resulted; the heat was then regulated so as to maintain gentle ebullition for about 30 minutes, the flame under the paraffin bath being adjusted so as to keep the temperature of the nitroglycerin practically constant. Determinations by the nitrometer showed that nitroglycerin that had been treated thus for some time had a much lower nitrogen content than the original nitroglycerin. To determine as fully as possible the extent to which decomposition without explosion could be brought about in nitroglycerin maintained at a temperature between that at which ebullition begins and that at which detonation takes place, the apparatus shown in figure 2 was used. Several cubic centimeters of nitroglycerin was placed in the small fractionating tube therein shown. The temperature of the paraffin bath was increased until active ebullition began, and was then maintained at this point for about 48 minutes. As a result, a small amount of distillate collected in the receiving tube. This

distillate and the residual nitroglycerin in the distilling flask were then collected and carefully examined.

The original nitroglycerin showed a nitrogen content of 18.45 per cent, whereas the residue left in the distilling flask, after being heated 48 minutes, showed a nitrogen content of 10.56 per cent. The distillate that collected in the receiving tube was observed to separate into two layers, one seemingly consisting of nitroglycerin, and the other mainly of dilute nitric acid. The distilled nitroglycerin was carefully separated from the acid water. It was found to be of a bright green color, and to be actively giving off nitrous fumes. At the expiration of about half an hour the distilled nitroglycerin ceased giving off nitrous fumes and became almost colorless. It was then washed with dilute sodium carbonate solution and with water, dried in a desiccator, and tested in the nitrometer. It showed a nitrogen content of 13.5 per cent. Tests made by heating this distilled nitroglycerin in a free flame and by percussion upon an anvil showed it still to be violently explosive. The undistilled residue left in the distillation tube possessed only very weak explosive properties, thus showing the extent to which the decomposition of the nitroglycerin had proceeded.

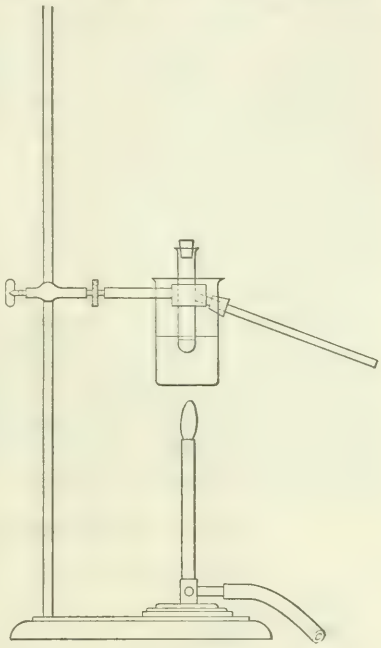

FIGURE 2.—Apparatus used in the distillation of nitroglycerin.

Preliminary experiments having shown that nitroglycerin could be heated to a temperature of 200° C. for considerable periods of time without explosion, it became necessary to determine why some of the former investigators had found that the explosion point of nitroglycerin was so much below this temperature. Careful experiments by Hagen,[a] carried out by immersing tubes containing nitroglycerin in a paraffin bath, the temperature of which, carefully tested by a thermometer, was 183.7° C., led to the belief that explosions were invariably brought about at this temperature. In the present series of experiments, however, in no case did nitroglycerin explode at a temperature below 200° C. Accordingly a very wide discrepancy is here apparent, for which an explanation should be found.

[a] Escales, Die Explosivstoffe, vol. 3, p. 160.

In the experiments made in heating nitroglycerin it was noted in many cases that the temperature of the nitroglycerin, as measured by the thermocouple, often continued to rise for a considerable length of time after the source of heat had been removed from beneath the paraffin bath. As the "lag" thus shown seemed to be far greater than could be accounted for by the transfer of heat by convection from the paraffin bath to the immersed tube containing nitroglycerin, it seemed probable that the decomposition of nitroglycerin, as evidenced by the ebullition taking place at temperatures above 145° C., was in reality a strongly exothermous reaction, and that therefore the tube of nitroglycerin might, in many experiments, be giving out heat to the bath instead of taking heat from it. To obtain definite information upon this interesting point, several experiments were carried out, in which the temperature in the paraffin bath and the temperature within the tube of nitroglycerin were simultaneously measured over a considerable range. It was found, as had been suspected from previous experiments, that the ebullition of nitroglycerin marks a form of decomposition which is accompanied by the evolution of much heat, and a tube of nitroglycerin immersed within a paraffin bath may attain a final temperature many degrees higher than the bath itself.

In one set of experiments a paraffin bath was heated to a definite temperature (164°C.), and the heat was so adjusted as to keep the bath at this temperature. A tube containing nitroglycerin (both the tube and the contained nitroglycerin being at room temperature) was then suddenly placed within the bath. The observations in this experiment were as follows:

Result of heating nitroglycerin in a bath at constant temperature.

Temperature of bath.	Temperature of nitroglycerin.	Observations.
°C.	°C.	
164	20	Tube containing nitroglycerin placed in bath. The temperature of the nitroglycerin rapidly rose, while the temperature of the paraffin bath dropped because of the transfer of heat from the paraffin to the cold tube and the nitroglycerin.
158	145	Ebullition of nitroglycerin began.
158	157	Violent ebullition.
160	163	
162	170	
163	173	
164	175	
165	177	
166	178	Nitroglycerin began to be thick and viscous.
167	179.5	
167.5	180	
167	178	
166	174	
165	171	
164	163	Total time of heating: 1 hour, 25 minutes. Sample converted to thick tarry dark-brown mass.

This experiment clearly proved the fact that the temperature of nitroglycerin contained in a tube kept in a bath at a temperature sufficient to initiate and maintain the active decomposition of the nitroglycerin, may rise many degrees higher than that of the bath by which the tube is heated. Hence all former results obtained by placing nitroglycerin in baths of paraffin or other substances and noting the temperature of the bath when the explosion occurred are practically without value.

EFFECT OF HEATING AT RISING TEMPERATURE.

In the experiment just outlined the amount of nitroglycerin taken (about 2 c.c.) and the initial temperature of the bath (164° C.) were so adjusted that the maximum temperature reached by the nitroglycerin (180° C.) was below the temperature at which detonation would be brought about. A second experiment was made with the initial temperature of the paraffin 80° C. at the time the nitroglycerin was introduced, and with a flame under the paraffin bath sufficient to cause the temperature of the bath to increase rapidly. In this experiment also it was found that the maximum temperature reached by the nitroglycerin was many degrees higher than that of the bath by which it was being heated. The reading of the thermometer in the nitroglycerin at the instant before explosion occurred was 215° C., this being about the same temperature that had been previously noted in other experiments as the temperature at which the explosion of nitroglycerin was invariably brought about, the explosion temperature in a series of experiments having been found to vary from 215° to 222° C. The notes of the experiment just mentioned are given in the following table:

Results of heating nitroglycerin in a bath of rising temperature.

Temperature of bath.	Temperature of nitroglycerin.	Observations.
° C.	° C.	
80	40	Started heating nitroglycerin.
120	87	
150	130	
174	148	Ebullition of nitroglycerin began.
180	165	Violent ebullition.
190	175	
145	185	Nitroglycerin thick and viscous.
196	190	
190	195	
198	205	
201.5	215	Violent detonation. (Total time of heating, 5 minutes.)

Several experiments having shown that nitroglycerin may become much hotter than the bath by which it is being heated, and that the bath temperature does not indicate the explosion temperature of

nitroglycerin, a number of experiments were made in which nitroglycerin was heated in tubes that contained in some cases a carefully calibrated thermometer, and in other cases a "constantan-copper" thermocouple. In all of the experiments thus carried out the results were almost uniform, the temperature at which ebullition began in nearly all the experiments being within two degrees of 145° C., and the temperature at which explosion occurred in all of the experiments being within two or three degrees of 218° C.

SUMMARY.

The results obtained through the series of experiments here outlined may be thus summarized:

Nitroglycerin begins to decompose at temperatures as low as 50° or 60° C. At a temperature of 70° C. nitroglycerin of commercial quality evolves enough nitrous fumes to give a decided test with potassium-iodide-starch paper at the expiration of 15 to 30 minutes. Moreover, nitroglycerin tends, even at very low temperatures, to be somewhat volatile, and it is well known that even at ordinary room temperatures nitroglycerin loses slowly in weight through volatilization. At somewhat higher temperatures both the decomposition and the evaporation of nitroglycerin increase. At a temperature of about 135° C. the decomposition of nitroglycerin is so rapid as to cause the liquid to become of a strongly reddish color, owing to the absorption of the nitrous fumes resulting from that which is decomposed; and at a temperature of about 145° C. the evolution of decomposition products is so rapid that, at atmospheric pressures, ebullition begins, and the liquid "boils" strongly. This "boiling" is due in part to the evolution of decomposition products (mainly oxides of nitrogen and water vapor) and in part to the actual volatilization of nitroglycerin itself.

The decomposition of nitroglycerin is accompanied by the evolution of much heat, and as soon as ebullition of a sample of nitroglycerin has begun, enough heat is generated within the liquid to rapidly raise the temperature of the mass, unless some means is provided for conducting away the heat evolved. At temperatures between 145° and 215° C. the ebullition of nitroglycerin becomes more and more violent; at higher temperatures the amount of heat produced by the decomposing liquid becomes proportionally greater, and at about 218° C. nitroglycerin explodes.

When nitroglycerin is maintained at a temperature between 145° and 210° C., its decomposition goes on rapidly, accompanied by much volatilization, and under these conditions nitroglycerin may be readily distilled. The distillate consists of nitroglycerin, nitric acid, water, and other decomposition products. The residue that remains

after heating nitroglycerin under such conditions for some time probably consists mainly of glycerin, with small amounts of dinitroglycerin, mononitroglycerin, and other decomposition products. These substances are far less explosive than ordinary nitroglycerin, and accordingly by heating nitroglycerin slowly it can be caused to "boil" away until the residue consists of products that are practically nonexplosive. In a number of experiments nitroglycerin was thus heated, and a copious residue was obtained. By carefully raising the temperature this residue could be made to char without explosion.

All temperatures found in this study were determined by thermometers or thermocouples immersed directly within the nitroglycerin. When thermometers were thus used, only those that had been checked with known standards were taken, and in all cases a table of corrections was applied. When thermocouples were used, the readings were checked against similar readings of the boiling points of liquids of known composition, such materials being selected for standardization as boiled at approximately the temperatures being measured in the experiment.

The temperature at which ebullition of nitroglycerin begins at normal atmospheric pressure was found to be 145° C. This result is correct within one or two degrees, although different samples of nitroglycerin naturally have somewhat different ebullition points, depending upon acidity, length of time of storage, etc. The temperature at which explosion is brought about (218° C.) should be accurate within about five degrees, differences being due, not to the method of testing, but to the individual variations of different samples of nitroglycerin.

It is the purpose of the authors to extend this work to cover the behavior of nitroglycerin when heated in the presence of normal constituents of dynamite, stabilizers, etc., and it is hoped that determinations may be made of the explosion points of a considerable number of organic nitrates and nitrosubstitution compounds.

PUBLICATIONS ON MINE ACCIDENTS AND TESTS OF EXPLOSIVES.

The following Bureau of Mines publications may be obtained free by applying to the Director, Bureau of Mines, Washington, D. C.

BULLETIN 17. A primer on explosives for coal miners, by Charles E. Munroe and Clarence Hall. 1911. 61 pp. 10 pls. Reprint of United States Geological Survey Bulletin 423.

BULLETIN 20. The explosibility of coal dust, by George S. Rice, with chapters by J. C. W. Frazer, Axel Larsen, Frank Haas, and Carl Scholz. 1911. 205 pp. 14 pls. Reprint of United States Geological Survey Bulletin 425.

MINERS' CIRCULAR 2. Permissible explosives tested prior to January 1, 1911, and precautions to be taken in their use, by Clarence Hall. 1911. 12 pp.

MINERS' CIRCULAR 3. Coal-dust explosions, by George S. Rice. 1911. 22 pp.

MINERS' CIRCULAR 4. The use and care of mine-rescue breathing apparatus, by J. W. Paul. 1911. 24 pp.

MINERS' CIRCULAR 5. Electrical accidents in mines; their causes and prevention, by H. H. Clark. 1911. 10 pp.

TECHNICAL PAPER 4. The electrical section of the Bureau of Mines; its purpose and equipment, by H. H. Clark. 1911. 13 pp.

TECHNICAL PAPER 6. The rate of burning of fuse as influenced by temperature and pressure, by W. O. Snelling and W. C. Cope. 1912. 28 pp.

TECHNICAL PAPER 7. Investigations of fuse and miners' squibs, by Clarence Hall and S. P. Howell. 1912. 19 pp.

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